

Explosives Handling and Stability Review Interval Program at LLNL

**D. W. Prokosch
R. L. Simpson
R. W. Swansiger**

February 1995



This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (615) 576-8401, FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

EXPLOSIVES HANDLING AND STABILITY REVIEW INTERVAL PROGRAM AT LLNL

Reviewed by:

D. W. Prokosch, LLNL HE Safety, Hazards Control

Reviewed by:

M. N. Tandy, Materials Management Group Leader

Reviewed by:

D. M. Hoffman, Formulation & Processing Group Leader
Explosives Development Committee Group I

Reviewed by:

C. O. Pruneda, Explosives Development Committee Group I

Reviewed by:

J. L. Maienschein, Initiation & Det. Performance Group Leader
Explosives Development Committee Group II

Reviewed by:

P. F. Pagoria, Synthesis Group Leader
Explosives Development Committee Group III

Reviewed by:

R.W. Swansiger, Explosives Development Committee Chair

Approved by:

R. L. Simpson,

Effective Date:

EXPLOSIVES HANDLING AND STABILITY REVIEW INTERVAL PROGRAM AT LLNL

Contents

- 1.0 Handling and Stability Review Program**
- 2.0 Policy Summary**
- 3.0 Purpose**
- 4.0 Guidelines**
 - 4.1 Handling Review Intervals**
 - 4.2 Establishing Handling Review Intervals**
 - 4.3 Establishing Handling Review Dates**
 - 4.4 Modification and Requalification of Handling Review Intervals & Dates**
 - 4.5 Stability Review Intervals, Dates, & Testing Dates**
 - 4.6 Establishing Stability Review Dates**
 - 4.7 Requalification or Extension of Stability Review Intervals & Dates**
 - 4.8 Transition to New Handling Review and Stability Review Procedures**

Appendices

- A. General Guidelines for Assigning Handling Review and Stability Review Intervals**
 - A.1 Stability Review Intervals for Bulk Propellants, Explosives and Other Nitrate Ester Containing Compounds**
 - A.2 Review Intervals for Single Materials and Formulations**
 - A.3 Review Intervals for Groups of Explosives**
- B. Recertification of Materials and Extension of Handling Review and Stability Review Intervals**

1.0 Handling and Stability Review Program

The response of explosives to mechanical, thermal or electrical input energy may change with time. This change may result in the failure of the explosive to perform as predicted during experimentation, mixing, pressing or machining. Such failure can produce a hazardous condition as well as a poor quality product. The hazards of handling or using degraded explosives and propellants may increase significantly. The Handling and Stability Review Program is established to prevent the inadvertent use of degraded explosives or propellants after storage. For the purpose of this procedure, "handling" is defined as any work performed on the explosive material involving significant input of energy, as determined by the Explosives Development Committee (EDC). Primary explosives will be evaluated and addressed by the EDC on a case-by-case basis.

2.0 Policy Summary

If an energetic material, e.g., an explosive or propellant, is known to degrade in a hazardous fashion during storage or contains stabilizers, a stability review interval shall be assigned to it which defines how often it is monitored. For energetic materials with inadequate data to determine long-term stability, a stability review interval shall also be assigned. Most LLNL materials will not have stability review intervals or dates.

A handling review interval shall be assigned to all explosives and propellants to ensure a material's pedigree prior to operations. If the handling review date has been exceeded, a review of the material's safety properties shall be made prior to carrying out operations involving the input of significant energy into the explosive material. Expiration of a handling review date does not imply that the material is unsafe to store and the term "handling review date" shall not be used in the context of storage.

The handling and stability review intervals shall be established through the peer review process of the EDC. As each material has unique properties, standardized testing is not applicable. However typical safety tests recommended for determining handling or stability review intervals include the chemical reactivity test (CRT), drop hammer, differential scanning calorimeter (DSC), friction and spark sensitivity.

3.0 Purpose

The purpose of this policy is to:

1. Define the Laboratory's program for establishing safe handling and stability review intervals for explosive materials. This program is applicable to all explosive materials in storage, in use, or received by the Laboratory.
2. Prevent the inadvertent use of degraded energetic materials.
3. Provide a list of common explosive materials used at LLNL and their assigned handling and (if applicable) stability review intervals. This listing (the "Explosives Storage and Interval Report") is maintained by Hazards Control Explosives Safety personnel, and copies are available from them.
4. Fulfill the requirement of the DOE Explosives Safety Manual (Chapter II, Section 17.3) which states that each DOE facility shall have a program to review the explosive materials stored at that facility.

This document supersedes Site 300 Procedure No. 118 Appendix C (Storage Review Intervals) and Facility Safety Procedure 222.10 (dated September 1, 1987) and Facility Safety Procedure 191, section 5.1.2.13.1. These procedures are effective as stated on the signature page of this document.

Exceptions to this policy may be made through the peer review process of the EDC, or by the Energetic Materials Section (EMS) Leader.

4.0 Guidelines

4.1. Handling Review Intervals

1. The previously used term "storage review date" shall no longer be used. The new term "handling review date" will be used in its place. Current policies referring to storage review shall be applied to handling review intervals. For the purpose of this procedure, "handling" is defined as any work performed on the explosive material (e.g. heating, mixing, machining, pressing). It does not include storage, shipping, weighing, packaging, inspection, radiography or other operations which do not involve the input of energy.

2. A handling review date shall be assigned to every explosive in use, in storage, or received by the Laboratory. The consignor or requester shall prepare the "Explosives Storage Review and Shipping Data" form for any material not previously listed in the Explosives Storage and Interval Report (see Section 3.3). That handling review interval must be reviewed by the peer review process of the EDC.
3. The handling review interval does not address storage stability or related storage issues. If a handling review date is exceeded, continued magazine storage is authorized, as there is no imminent hazard associated with storage. No action is required until the material is to be "handled". Magazine operators shall not control materials on the basis of handling review dates, except as described below.
4. Material which has passed its handling review date may be removed from the magazine in quantities up to 5 grams for safety testing. The label and shipping tag shall be marked "For Safety Tests Only". Larger quantities may be released for use in operations not involving significant energy input. If larger quantities are to be used in operations involving energy input, a Peer Review stating the conditions for use must be approved by both the usual EDC signatures and the EMS Leader.

4.2 Establishing Handling Review Intervals

1. When a material is produced under a peer reviewed procedure, the handling review interval will be established in that document. See Appendices A.2 and A.3 for further instructions.
2. If the handling review interval is unknown or not stated, an interval of 90 days shall be used.
3. The handling review interval may be modified (extended or shortened) by the peer review process of the EDC, or by the EMS Leader.

4.3 Establishing Handling Review Dates

1. The handling review date shall be established by adding the handling review interval to the date of manufacture, if known, or the date the material is received at the Laboratory. The handling review date shall be shown on or adjacent to the identification tag or Explosives ID Label on every container or package of explosives in use or storage.
2. The handling review date for pressed billets and parts made from molding powder will be the same as for the original source material.

4.4 Modification and Requalification of Handling Review Intervals/Dates

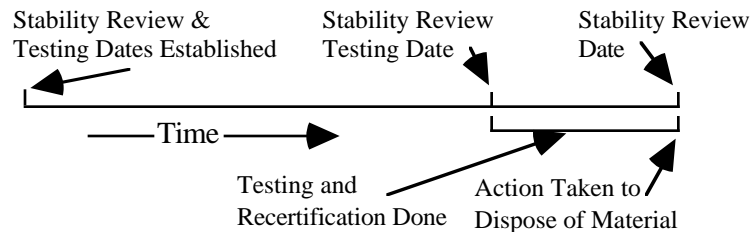
1. When a material exceeds its handling review date, a new handling review date shall be established using the processes described in Section 4.2 and Appendix B before the material can be "handled". Until a new date is established, operations with that material that involve input of significant mechanical, electrical, or thermal energy as determined by the EDC shall be done under a Peer Review where aging effects are considered. Exceptions include:
 1. Destroying the material. However, materials in UNO Storage Compatibility Group L in quantities >50gm require peer review before disposal.
 2. Small-scale safety tests required to establish a new handling review date.
 3. Operations in which quantities are ≤ 50 mg with secondary explosives.
 4. Operations in which the possible input of energy required to initiate the material is negligible, e.g., dissolution in synthesis operations where the heat of solution is neutral or endothermic.

4.5 Stability Review Intervals, Dates & Testing Dates

1. A stability review interval, date, and testing date shall be given to materials that contain stabilizers, become unstable as they age, or have unknown stability hazard properties. Older policies referring to "surveillance review dates" (or intervals) shall be treated as

"stability review dates" (or intervals). When a material is produced under a Peer Review, the stability review interval will be established in that document. When a material is received on site, the stability review interval will be established on the "Explosives Storage and Shipping Data" form.

- 2.0 Stability review intervals are not required for all materials. The vast majority of materials at LLNL will not require stability review intervals.
- 3.0. A stability review testing date shall be given to materials requiring a stability review date. This testing date shall be used by magazine operators as a warning that a stability review date is approaching and that the testing and review process should begin. Stability review testing dates shall be at least one month before the stability review date, to allow time for testing and review to be completed. The test data will be peer reviewed by the EDC or the EM Section Leader to decide whether the material should be recertified for a new time interval, have more stabilizer added (if feasible), or be destroyed.



4. If a material exceeds its stability review date, it shall immediately be brought to the attention of the EDC, which will decide whether the material must be destroyed at once or whether it may be submitted for testing and recertification. Technical safety issues shall be paramount during the disposal process. Safety shall not be compromised in the effort to dispose of the material rapidly.
5. Samples stored in 10 gram non-propagating arrays are exempt from stability review date procedures. Samples of <50g which are part of an ongoing experimental investigation, e.g., part of a synthetic scheme, are also exempt. Their purity will be verified by spectroscopic means prior to use.

4.6. Establishing Stability Review Dates

1. When a material is produced under a peer reviewed procedure, the stability review interval, date, and testing should be established in the Peer Review.
2. The stability review and testing dates may be modified with the "Explosives Storage and Shipping Data" form, or other documents which are peer reviewed by the EDC, or by the EM Section Leader.

4.7 Requalification or Extension of Stability Review Intervals & Dates

Appendix A.1 contains the specifics of the testing procedures for stability. The EDC shall review the test results to determine the disposition of the material and determine the new interval, date, etc. Appendix B details the recertification process.

4.8 Transition to New Handling Review and Stability Review Procedures

1. These new procedures are effective as stated on the signature page of this document.
2. Immediate relabeling of materials currently in storage is not required.
 1. Materials in storage labeled with storage review dates shall be treated as if they were handling review dates.
 2. When a material is removed from storage, it shall be relabeled at that time using the new Explosives ID label and handling review date nomenclature.
 3. Materials that are transported on site shall have the appropriate handling review date and stability review date information on the Explosives ID label.

3. Materials not requiring stability review dates shall not be arbitrarily assigned one. Stability dates are not required if the material is known to be indefinitely stable under storage conditions, or if it decomposes in a non-hazardous fashion to non-hazardous products. When a stability review date is requested on a form or identification label but does not apply to the material, write "NA" (not applicable) in the space.

Appendix A

General Guidelines for Assigning Handling Review and Stability Review Intervals

A.1 Stability Review Intervals for Bulk Propellants, Explosives and Other Nitrate Ester Containing Compounds

- A. Energetic materials containing nitrate esters such as nitrocellulose vary widely in stability. They commonly contain a decomposition inhibitor (stabilizer) which is gradually neutralized internally; when the inhibitor is sufficiently depleted, decomposition accelerates. Decomposition has led to incidents and spontaneous ignition of large masses of propellant. A surveillance system for designated nitrate esters and bulk propellants in storage is necessary. Nitrate esters, propellants and other energetic materials that are a part of this surveillance program shall have handling review intervals and dates in addition to their stability review intervals and dates. In some cases these may be identical.
- B. Bulk energetic materials in quantities greater than 2.5kg containing nitrocellulose, nitroglycerine, or other nitrate esters in storage at Site 300 shall be tested and reviewed for stability. All new energetic material formulations larger than 50gm containing nitrocellulose, nitroglycerine, other nitrate esters, or stabilizers must be assigned a stability review interval. It is the responsibility of the Magazine Custodian to maintain surveillance testing of all designated nitrate esters and bulk energetic materials. One sample from each lot, batch, etc., will be designated as a control item and will be inspected annually. Surveillance testing shall consist of inserting a dated strip of tenth-normal methyl violet indicator paper in each designated control item container. (Pencil dating is preferred to ink because of superior permanence) The indicator shall be inspected at least once a year for bleaching and replaced by a fresh strip. A change in color of the methyl violet indicator is indicative of significant deterioration, and the propellant in that container shall be removed from storage and disposed of. All containers of the same lot or batch shall be checked, and those failing the inspection destroyed.
- C. Nitroglycerin and other liquid nitrate esters shall be tested for stability every six months. Material that fails testing shall be destroyed promptly. The testing consists of the following:

1. A check for the formation of NO_X using an iodine paper test strip. If NO_X is detected, no further testing should be performed until further actions are approved by the EDC and Hazards Control Explosives Safety.
2. Quantitative measurement of the acidity of the solution. If acid is detected, the material shall be immediately destroyed.
3. Quantitative measurement of the amount of stabilizer remaining. If the stabilizer is below acceptable levels, additional stabilizer may be added or the material must be destroyed.

A.2 Review Intervals for Single Materials and Formulations

- A. Those compounds and formulations for which LLNL personnel have much information and/or experience should be assigned a handling review interval commensurate with that information and/or experience.
- B. If the material is unfamiliar (e.g., new compound, new commercial formulation, etc.) assign a handling review interval of 90 days.
- C. A freshly made batch of a formulation with known properties acquires the nearest handling review date of its components unless appropriate tests show that a different handling review interval is justified.
- D. If the compound or formulation is new to LLNL, but other DOE contractors or DOD agencies have extensive experience, use DOE contractor or DOD information conservatively in assigning a handling review interval.
- E. For a new formulation of known composition, assign a conservative handling review interval based on the least stable component.
- F. Commercial slurry blasting formulations must be treated with respect. Their physical and chemical stability must be questioned. Segregation of components may give rise to safety problems during prolonged storage. a conservative handling review interval should be assigned.

- G. Finely divided metal/fluorocarbon mixtures should be given a handling review interval of 90 days initially.
- H. Fluorodinitro and gem-dinitro compounds are suspect. Assign a one year handling review interval unless experience indicates that a longer (or shorter) life is justified. The same applies to solutions of these materials.
- I. If a manufacturer has assigned a shelf life for a formulation, the review interval shall not exceed the recommended shelf life. However, the interval may be renewed for the same or shorter time if appropriate tests and review indicate that the material can be used safely. A material need not necessarily be disposed of upon expiration of the manufacturer's recommended shelf life.
- J. If no information is provided with the request for storage for a new material, do not assign a handling review of more than 90 days.
- K. In many cases, storage containers and environment are important. They must be taken into account when assigning a handling or stability review interval.
- L. Trinitroethyl compounds and liquid nitrate esters should be assigned a stability review interval of no more than 90 days initially.
- M. Solutions of an explosive in a desensitizing volatile solvent may have two stability issues: one related to the possible loss of solvent and a second related to the stability of the explosive. The fluid level should be marked on the container and dated at the time of storage. Select a stability review interval based on whichever issue is expected to arise first; monitor both issues at the same time.

A.3 Review Intervals for Groups of Explosives

- A. These guidelines cover cases in which the subject material is intended to include a range of compositions as opposed to a single definite composition.
- B. Several similar formulations (i.e., several RX numbers) may be included on the same "Explosives Storage Review and Shipping Data" form. Alternatively, the explosive composition may be stated as a variable weight fraction of the ingredients in order to include similar compositions covering a range of proportions of the ingredients. The ranges of proportions shall be stated.

- C. The same ingredients shall be present in all compositions of the group. (This is especially important if a stabilizer or desensitizer is present).
- D. The range of compositions should have reasonably narrow bounds such that one can estimate the minimum chemical stability and impact sensitivity of all possible members of the group from the data supplied.
- E. Safety and reactivity data shall be supplied for at least one member of the group. If an estimate of the properties of the rest of the group, especially the least stable possibility, is uncertain, more data should be provided to better cover the range.
- F. The purpose of combining more than one experimental formulation is to provide a storage review interval for several similar experimental materials for which complete data sets have not been measured and appear to be unnecessary. The method may also be used to cover a family of similar variants of a characterized material which have not been made. In order to prevent loss of control over untested explosives, it is important that the formulations in a group be reasonably similar and that composition bounds are not excessively wide. Good judgment is more reliable than any simple numerical scheme for selecting these composition bounds; however, $\pm 50\%$ of the nominal value for each ingredient is typically a sufficiently wide range. The following is an example of the $\pm 50\%$ variation.

<u>Ingredient</u>	<u>Nominal</u>	<u>Composition, wt %</u>	
		<u>Maximum, +50%</u>	<u>Minimum, -50%</u>
A	8	12	4
B	20	30	10
C	72	100*	36*
		(86)	(58)

* Not accessible because other ingredients would fall outside the permitted range. Values in () are the maximum range of C that is compatible with the limits on A and B.

Appendix B

Recertification of Materials and Extension of Handling and Stability Review Intervals

- B.1 If the currently approved handling or stability review interval is longer than the one originally applied to a generic material, the previous review data may be revised to be consistent with the current review interval. No retesting or approval is needed.
- B.2 Recertification of a material whose review date has expired should be on a lot or batch basis by retesting and reviewing each lot or batch. Extensions do not apply automatically on a generic basis.
- B.3 Recertification of a material after retesting and review may be for a different review interval than initially assigned, either longer or shorter, at the discretion of the EDC. This is an important way to use experience with a material in estimating a more realistic safe life. If a material shows no significant change or degradation after storage for a time much longer than the current review interval, it may be assigned a new review interval. The renewal may be for a more generous interval.
- B.4 The most important consideration in a review is the changes in properties of the material during its life. Thus, it is important to establish as good a data file of measured properties as is practical on a material as soon as possible after it is made.
- B.5 Purification of a material normally resets its clock at zero, and the handling review interval remains the same. No specific approval action is needed for the extension of the review date. Characterization tests should be performed for comparison with future tests for subsequent storage review. This does not apply to stability review intervals/dates.

Technical Information Department • Lawrence Livermore National Laboratory
University of California • Livermore, California 94551
